CHAPTER 7

Half-sandwich d⁶ metal complexes with bis(pyridine carboxamide)benzene ligand: Synthesis and spectral analysis

7.1 Introduction

7.2 Experimental section

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Graphical Abstract

Mono- and bi-nuclear half-sandwich d$^6$ metal complexes with bis(pyridine carboxamide)benzene ligand have been synthesized and characterized. Complexes 2-6 are additionally studied by single crystal x-ray analysis. Complexation occurred by the deprotonation of the amidato nitrogen of the ligand by using the base sodium methoxide (NaOMe). The effect of base has not influenced in the case of heavier congener.

Abstract

The reactions of [(arene)MCl₂]₂ dimers with the 1,4-bis(2-pyridine carboxamido)benzene (H₂L) have been reported here with the formulations as [(arene)MCl(HL)] \{where, arene = p-cymene, M = Ru (1), arene = Cp*, M = Rh (2) and Ir (3)\} and \{(arene)MCl₂L\} \{where, arene = p-cymene, M = Ru (4), arene = Cp*, M = Rh (5) and Ir (6)\}, which resulted in a series of mono- and di-nuclear neutral complexes. These complexes have been characterized by various spectral analyses. Complexes 2-6 are additionally described by the single crystal X-ray diffraction studies. Single crystal X-ray analyses of complexes showed that they are neutral in nature and vicinity around the metal is distorted octahedral. The chloride atoms and Cp* moieties are in cis orientation with respect to the ligand in the case of complex 6. Complexes 2, 3 and 5 are crystallized with the solvent dichloromethane molecule.

Key words: 1,4-bis(2-pyridine carboxamido)benzene, ruthenium, rhodium, iridium.
7.1. Introduction

The investigation of pyridine carboxamide ligands with the biologically relevant transition metals has drawn much attention for their amide functional group [1-3]. The facility of the amide functional group offers the ligands to coordinate metal either by nitrogen of amidato or by oxygen of carbonyl group [4, 5]. Complexes with such a difference in bonding towards the metal offer a coordination isomerism such as linkage isomerism [6-8]. Some of the amidato nitrogen bound complexes shown significant activity over colon, ovarian and cisplatin-resistant ovarian human cancer cell lines. In the case of carbonyl oxygen bound complexes are non-toxic [9]. Some of these carboxamide-derived complexes have studied for the production of nitric oxide (NO) to specific cellular targets, such as nitric oxide synthase (iNOS), which results in the cell death in the cancer cells [10-12].

Since the discovery of cisplatin in the 1960’s and subsequent activity over certain cancer cells offers the great interest of metal complexes towards the biological systems [13]. Since that time, it has drawn much attention in the metal-based anticancer drugs with limited or no side effects and an activity on cis-platin-resistant cancer cells [14-17]. Such a challenge has been made to focus on many metal-based complexes among them organometallic 8th and 9th group metal complexes possess a better activity over cis-platin-resistant cancer cell lines with a different mechanism of action [18]. Many organometallic half sandwich d6 metal complexes have been well researched with the biologically active [19, 20] and or inactive ligands [21], whereby few of them reached to evaluate for clinical trials [22-24]. When it comes to carboxamide ligands with the half sandwich metal complexes very few reports are available. McGowan and his group members have observed that these carboxamide-derived complexes have shown some promising results and in some cases, they resulted good cytotoxicity than the anticancer drug cisplatin [25-29]. Hartinger et al., observed the cytotoxicity of the carboxamide ligands with 8th group metal complexes, which are not active even after 72 h incubation period over human colon (HCT116, SW480), non-small cell lung (NCI-H460), and cervical (SiHa) carcinoma cell lines [30].

Recently our group also focused on hydrazone based complexes where the carboxamide moiety plays a central role as chemically with the diverse bonding modes [31] and as biologically with their selectivity towards cancerous cell and bacterial strains on complexation [32-34]. In this manuscript, we aim to synthesis and structural characterization
of six new mono and di-nuclear arene d₆ metal {ruthenium, rhodium and iridium} complexes of bis(pyridine carboxamide)benzene (H₂L) ligand (Chart 7.1).

![Chart 7.1: Ligand (H₂L) used in the present study](image)

### 7.2. Experimental

#### 7.2.1. Materials and methods:

Metal halides RuCl₃·xH₂O, RhCl₃·xH₂O, IrCl₃·xH₂O (Arora Matthey Ltd), α-terpinene, pentamethycyclopentadiene (Sigma-Aldrich), 1,4-Phenaline diamine (Loba Chemie) and 2-picolinic acid (Spectro Chem) were purchased and used as received. Starting precursors [(p-cymene)RuCl₂]₂, [{Cp*RhCl₂}]₂ and [{Cp*IrCl₂}]₂ and ligand H₂L were prepared according to the literature methods [35-38].

#### 7.2.2. Procedure for the syntheses of mono and di-nuclear complexes 1-6.

A mixture of [(arene)MCl₂]₂ (where arene = p-cymene, M = Ru; arene = Cp*, M = Rh/Ir) (0.08 mmol) and ligand H₂L (0.16 mmol for mono-nuclear and 0.08 mmol for di-nuclear) were taken in chloroform and methanol 1:1 ratio (30 ml) in presence of base (sodium methoxide; 0.16 mmol for mono-nuclear and 0.08 mmol for di-nuclear). The mixture was refluxed for 4-6 hours during which the color of the solution changed from red to an orange color. These solutions were filtered through the bed of celite to remove insoluble materials. The orange solutions were concentrated to 5 ml and addition of hexane resulted an orang-yellow precipitate of the complexes. These precipitates were washed with diethyl ether and air-dried.

#### 7.2.2.1. [(p-cymene)RuCl(HL)] (1)

Yield: 46 mg (49%), IR (KBr pellets, cm⁻¹): 3340 ν(N⎯H), 1671 ν(C=O), 1616 ν(C=O), 1583 ν(C=N), 1469 ν(C=CH); ¹H NMR (400 MHz, CDCl₃) δ 10.02 (s, 1H), 8.95 (d, J = 5.1 Hz, 1H), 8.58 (t, J = 5.7 Hz, 1H), 8.26 (t, J = 5.5 Hz, 1H), 8.03 (t, J = 5.7 Hz, 1H), 7.91 – 7.84 (m, 2H), 7.78 (s, 2H), 7.68 – 7.66 (d, J = 5.9 Hz, 2H), 7.44 (dt, J = 8.3, 4.3 Hz, 1H), 5.59 (d, J = 6.0 Hz, 1H), 5.51 (d, J = 6.1 Hz, 1H), 2.51 (sep, 1H), 2.17 (d, J = 6.3 Hz, 6H), 2.12 (s, 3H); UV-Vis
{Acetonitrile, λmax, nm (ε, 20 μM⁻¹ cm⁻¹)}: 317 (1.1 × 10⁴), 254 (0.9 × 10⁴), 201 (3.5 × 10⁴); ESI-MS (m/z): 553.12 [M-Cl].

7.2.2.2. [Cp*RhCl(HL)] (2)

Yield: 60 mg (63%), IR (KBr pellets, cm⁻¹): 3344 ν(N-H), 1669 ν(C=O), 1614 ν(C=O), 1583 ν(C=O), 1469 ν(C=N); ¹H NMR (400 MHz, CDCl₃) δ 10.07 (s, 1H), 8.63 (d, J = 4.7 Hz, 1H), 8.31 (t, J = 7.8 Hz, 1H), 8.17 (d, J = 7.6 Hz, 1H), 7.94 (dt, J = 15.1, 7.6 Hz, 2H), 7.83 (s, 2H), 7.79 (t, J = 10.8 Hz, 1H), 7.50 (dd, J = 7.5, 4.6 Hz, 2H), 1.43 (s, 15H, Cp*); UV-Vis {Acetonitrile, λmax, nm (ε, 20 μM⁻¹ cm⁻¹)}: 316 (0.91 × 10⁴), 258 (0.96 × 10⁴), 203 (4.27 × 10⁴); ESI-MS (m/z): 555.12 [M-Cl].

7.2.2.3. [Cp*IrCl(HL)] (3)

Yield: 52 mg (48%), IR (KBr pellets, cm⁻¹): 3340 ν(N-H), 1672 ν(C=O), 1619 ν(C=O), 1586 ν(C=O), 1466 ν(C=N); ¹H NMR (400 MHz, CDCl₃) δ 10.03 (s, 1H), 8.63 (d, J = 4.7 Hz, 1H), 8.59 (d, J = 5.2 Hz, 1H), 8.31 (d, J = 7.8 Hz, 1H), 8.17 (d, J = 7.1 Hz, 1H), 7.97 – 7.88 (m, 2H), 7.84 (s, 2H), 7.76 (d, J = 8.8 Hz, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.53 – 7.45 (m, 2H), 1.43 (s, 15H, Cp*); UV-Vis {Acetonitrile, λmax, nm (ε, 20 μM⁻¹ cm⁻¹)}: 318 (1.69 × 10⁴), 256 (1.77 × 10⁴), 205 (4.39 × 10⁴); ESI-MS (m/z): 645.18 [M-Cl].

7.2.2.4. [{(p-cymene)RuCl₂L}] (4)

Yield: 38 mg (40%), IR (KBr pellets, cm⁻¹): 1616 ν(C=O), 1583 ν(C=O), 1498 ν(C=N); ¹H NMR (400 MHz, CDCl₃) δ 8.96 (d, J = 5.64 Hz, 2H), 8.06 (d, J = 7.9 Hz, 2H), 7.90 (t, J = 7.6 Hz, 2H), 7.73 (s, 2H), 7.68 (s, 2H), 7.44 (t, J = 7.5 Hz, 2H), 4.85 (d, J = 6.0 Hz, 4H), 4.76 (d, J = 5.8 Hz, 4H), 2.61 – 2.49 (sep, 2H), 2.15 (s, 6H), 1.04 (d, J = 1.7 Hz, 12H); UV-Vis {Acetonitrile, λmax, nm (ε, 20 μM⁻¹ cm⁻¹)}: 318 (1.01 × 10⁴), 254 (1.68 × 10⁴), 206 (6.64 × 10⁴); ESI-MS (m/z): 790.12 [M-RuCl₂].

7.2.2.5. [{Cp*RhCl₂L}] (5)

Yield: 45 mg (64%), IR (KBr pellets, cm⁻¹): 1612 ν(C=O), 1579 ν(C=O), 1496 ν(C=N); ¹H NMR (400 MHz, CDCl₃) δ 8.67 (d, J = 4.9 Hz, 2H), 8.35 (d, J = 9.5 Hz, 2H), 7.97 (t, J = 7.8 Hz, 2H), 7.88 (s, 4H), 7.54 (t, J = 7.7 Hz, 1H), 1.48 (s, 30H, Cp*); UV-Vis {Acetonitrile, λmax, nm (ε, 20 μM⁻¹ cm⁻¹)}: 315 (0.69 × 10⁴), 255 (1.54 × 10⁴), 203 (3.47 × 10⁴); ESI-MS (m/z): 792.14 [M-Cl].
7.2.2.6. [{Cp*IrCl}2L] (6)

Yield: 54 mg (65%), IR (KBr pellets, cm⁻¹): 1619 ν(=O), 1585 ν(=C), 1499 ν(=N); ¹H NMR (400 MHz, CDCl₃): δ 8.65 (d, J = 5.2 Hz, 2H), 8.32 (d, J = 7.8 Hz, 2H), 7.91 (t, J = 7.8 Hz, 2H), 7.65 (s, 4H), 7.55 – 7.43 (m, 2H), 1.71 (s, 30H, Cp*); UV-Vis {Acetonitrile, λmax, nm (ε, 20 μM⁻¹ cm⁻¹)}: 322 (0.72 × 10⁴), 262 (0.98 × 10⁴), 204 (5.11 × 10⁴); ESI-MS (m/z): 1006.65 [M-Cl]⁺, 970.25 [M-Cl₂]⁺.

7.3. RESULTS AND DISCUSSION

7.3.1. Synthesis of complexes 1-6

Carboxamide ligand has derived from 2-picolinic acid and p-pheneline diamine in presence of the coupling agent triphenylphosphite. Ligand has limited solubility in common organic solvents except chloroform due to that all the complexes has prepared in a mixture of solvent system i.e., chloroform and methanol as 1:1 ratio. Reactions of chloro bridged d⁶ metal (Ru, Rh and Ir) precursors with the ligand (H₂L) in presence of base (NaOMe) as 1:2:1 ratio yielded mononuclear complexes whereas 1:1:1 ratio yielded di-nuclear complexes (Scheme-7.1). Complexes are obtained as orange red powders and these are air stable. All these complexes are soluble in common polar organic solvents like DCM, chloroform, acetone, methanol and acetonitrile but are insoluble in nonpolar solvents such as hexane, diethyl ether and petroleum ether.

![Scheme 7.1: Synthesis of metal complexes 1-6 with ligand (H₂L)](image-url)
7.3.2. Characterization of the complexes

IR, $^1$H NMR and UV-Vis spectroscopy used to characterize these complexes. The analytical data of these complexes are consistent with the formulations. Infrared spectra of all these complexes exhibit sharp bands due to chelating ligand, H$_2$L in between 3340 cm$^{-1}$ and 1466 cm$^{-1}$. The stretching frequency of N─H around 3340 cm$^{-1}$ in the mono-nuclear complexes 1-3 with a slight blue shift compared to the free ligand (H$_2$L) 3338 cm$^{-1}$ while in the di-nuclear complexes such a peak has not been observed. In addition to this all the complexes display strong carbonyl stretching frequencies (ν$_{C=O}$) in the range 1674-1612 cm$^{-1}$, which are red shifted in the di-nuclear complexes with a stretching frequency around 1616 cm$^{-1}$. While in mono-nuclear complexes two kinds of stretching frequencies values with a slight blue (1673 cm$^{-1}$) and strong red shifts (1616 cm$^{-1}$) has been observed in comparison to the stretching frequency (ν$_{C=O}$) value of the free ligand 1668 cm$^{-1}$ [39]. This conforms coordination of ligand in the deprotonation forms of these mono and di-nuclear complexes.

$^1$H NMR spectral data of these complexes exhibited that the ligand peaks (Fig. 7.1) are shifted in the downfield region as compared to that of the free ligand suggesting coordination of the pyridyl nitrogen atoms to the metal center in a regular fashion. The absence of N─H proton in di-nuclear complexes and its presence in mononuclear complexes with a slight shift with respect to the free ligand suggests that the bonding occurred by the deprotonation of the amide nitrogen. The $^1$H NMR spectra of these complexes also exhibited metal precursor protons with a variable shift than the starting dimers. The integral ratio and number of multiplet peaks of the protons in mono- and di-nuclear complexes are distinguishable. For instance, the ratio between bonded, unbounded and precursor protons is 1:1:1 in mononuclear complexes (Fig. 7.2), whereas in di-nuclear complexes the ratio between bonded and precursor protons is 1:1 (Fig. 7.3 and 7.4). In mononuclear complexes 1-3 protons of the ligand H$_2$L resonated at δ 10.02 (s), 8.95 (d), 8.58 (t), 8.26 (t), 8.03 (t), 7.91 – 7.84 (m), 7.78 (s), 7.68 – 7.66 (d) and 7.44 (dt) ppm, which indicates that the bonding occurred unsymmetrically to the metal atoms in a symmetrical ligand. Whereas in di-nuclear complexes 4-6, the ligand peaks resonated as 8.96 (d), 8.06 (d), 7.90 (t), 7.73 (s), 7.68 (s) and 7.44 (t) ppm such a multiplet analysis clearly indicates that the bonding occurred symmetrically to the metal atoms in a symmetrical ligand as by the loss of the amidinato proton.
Fig. 7.1: $^1$H NMR spectrum of the ligand (H2L).

Fig. 7.2: $^1$H NMR spectrum of the complex-1.
Fig. 7.3: $^1$H NMR spectrum of the complex-4.

Fig. 7.4: $^1$H NMR spectrum of the complex-5.
Mass spectral analysis of these neutral complexes has been recorded in acetonitrile and the m/z values are given in the experimental section and the spectra presented in Fig. 7.5-7.9. ESI-MS spectra of mono-nuclear complexes (1-3) showed prominent peaks at m/z 553.12, 555.12 and 645.18 respectively by the loss of chloride ion, corresponding to [(p-cymene)Ru(HL)]⁺ (Fig. 7.5), [Cp*Rh(HL)]⁻ (Fig. 7.6) and [Cp*Ir(HL)]⁺ (Fig. 7.7) ions which are consistent with the expected formulations. Whereas in di-nuclear complexes (4-6) also shown prominent peaks at m/z 790.12, 792.14 and 970.25 respectively by the loss of both labile chloride ions which corresponding to [{(p-cymene)Ru₂L}⁺, [{Cp*Rh₂L}⁺ (Fig. 7.8) and [{Cp*Ir₂L}⁺ (Fig. 7.9) respective ions.

Fig. 7.5: ESI-MS spectrum of the complex-1.
Fig. 7.6: ESI-MS spectrum of the complex-3.

Fig. 7.7: ESI-MS spectrum of complex-4.
Fig. 7.8: ESI-MS spectrum of the complex-5.

Fig. 7.9: ESI-MS spectrum of the complex-6.
7.3.3. UV-Visible spectroscopy:

The electronic spectra of the complexes 1-6 along with the ligand (\( \text{H}_2\text{L} \)) were acquired in acetonitrile at 20 μM concentration and are depicted in Fig. 7.10. The free ligand exhibited three characteristic bands at an around 208 (75495), 250 (9775), 321 (19195). On complexation, the bands of the free ligand (\( \text{H}_2\text{L} \)) exhibited some blue shift in addition to that some low intense bands have been appeared in the visible region (~ 400-450 nm) of the spectrum of the complexes. These new bands are attributable to the metal-to-ligand charge transfer (MLCT) \( \text{t}_{2g} \rightarrow \pi^* \) transition in their electronic spectra [40, 41]. These low intense broad bands are obscured by the ligand-centered high intense bands or may be affected by the low concentrated (20 μM) solutions. The electronic spectra of these complexes display a characteristic hypochromism in the medium and high-intensity bands with a slight blue shift. The bands on the higher energy side at ~ 320-200 nm for these complexes have been assigned to ligand-centered \( \pi \rightarrow \pi^* \) transitions [33, 42]. In general, these complexes follow the normal trends observed in the electronic spectra of the nitrogen-bonded metal complexes, which display a ligand-based \( \pi \rightarrow \pi^* \) transition for carboxamide ligands in the UV region and metal-to-ligand charge transfer transitions in the visible region.

![Fig. 7.10: UV-Visible spectra of the complexes 1-6 along with the ligand H₂L with a concentration of 20 μm at room temperature.](image-url)
7.3.4. Molecular structures

Single red and yellow crystals suitable for X-ray crystallographic analysis were obtained for complexes 2-6. Which are grown by layer diffusion with a DCM, Acetone/hexane solvent system mono-nuclear complexes (2 and 3) crystallizes in the triclinic system and are solved in the space group $P\overline{1}$ with 2 and 1 molecules in a unit cell respectively. While di-nuclear complexes 4, 5 and 6 crystallizes in either monoclinic (4 and 5) or orthorhombic (6) systems and is solved in the space group $P2_1/c$, $P2_1/n$ and $Cmc2_1$ with 2, 4 and 4 molecules in a unit cell respectively. ORTEP drawings with the atom-labeling scheme for these complexes are shown in Fig. 7.11-7.13. Crystal data and data collection parameters for the complexes 2-6 are summarized in Table 7.1 while selected bond distances and angles are listed in Table 7.2. PLATON program is used to squeeze the disordered hexane and water molecules in complex 4 and 6 respectively.

The overall geometry of these complexes exhibits a pseudo-octahedral three-legged piano-stool geometry around the metal center whereby the arene ($p$-cymene/Cp*) occupies three coordination sites as a seat of the stool. The complexes are containing one metal center, $\pi$-bonded to arene, $\sigma$-bonded to a chloride and a symmetry related ligand ($\text{HL}$), which is coordinated by the bidentate $\text{NN}^-\text{N}$ mode through the pyridine nitrogen atom and the amido nitrogen ion instead of neutral amide nitrogen or carbonyl oxygen. These nitrogen atoms and chloride atom constitute the remaining three coordination sites as legs of the stool. In mono-nuclear complexes the distance between the metal atom and the centroid of the arene ring is 1.794 Å in complex 2 and 1.785 Å in complex 3 whereas the corresponding metal to centroid of the arene distances in di-nuclear complexes 4-6 are $\text{v}iz.$, 1.676 Å, 1.791 Å, and 1.778 Å which are shorter than that of mono-nuclear complexes 2 and 3. However, the geometrical parameters for these neutral complexes are comparable to those in related complexes [41, 43]. The M-N(1) and M-N(2) distances in these complexes are in inconceivable variation, where pyridine nitrogen bonded with a shorter distance compared to the amidinato nitrogen. Surprisingly in iridium di-nuclear complex, such distances are altered where pyridine nitrogen bonded with larger distance than the amidinato nitrogen, which might be due to the cis orientation of the molecule. The metal to chloride bond lengths in complexes 2-6 is 2.4189(9), 2.4149(10) 2.4081(13), 2.4237(9) and 2.401(3) respectively which are closely similar to the reported carboxamide moiety contained metal complexes [44]. All the complexes exhibit intermolecular hydrogen bonding, which enhances the stability to the molecular geometry and in some complexes, solvent (DCM) molecule also played a role.
Table 7.1: Crystallographic and structure refinement parameters for complexes 2-6.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Chemical Formula</th>
<th>Formula Mass</th>
<th>Crystal system</th>
<th>a/Å</th>
<th>b/Å</th>
<th>c/Å</th>
<th>α°</th>
<th>β°</th>
<th>γ°</th>
<th>Unit cell volume/Å³</th>
<th>Temperature/K</th>
<th>Space group</th>
<th>Z</th>
<th>Index ranges</th>
<th>D, (g.cm⁻³)</th>
<th>μ (mm⁻¹)</th>
<th>F(000)</th>
<th>0 Range</th>
<th>Reflections collected</th>
<th>Independent reflections</th>
<th>Absorption correction</th>
<th>Data/restraints/parameters</th>
<th>Goodness-of-fit on F²</th>
<th>Final R indices [I&gt;2σ(I)]*</th>
<th>R indices (all data)</th>
<th>Max, Min Δρ/e (Å⁻³)</th>
<th>CCDC No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>C₃₆H₃₁N₄O₄:Rh.C₂H₂Cl₂</td>
<td>675.83</td>
<td>Triclinic</td>
<td>7.9112(4)</td>
<td>14.6002(6)</td>
<td>14.6994(8)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>1455.81(12)</td>
<td>293.3(3)</td>
<td>P1₁</td>
<td>2</td>
<td>-9 ≤ h ≤ 8, -19 ≤ k ≤ 18, -17 ≤ l ≤ 18</td>
<td>1.542</td>
<td>0.896</td>
<td>688</td>
<td>3.23 to 28.99</td>
<td>10142</td>
<td>6543 [R(int) = 0.0294,]</td>
<td>Semi-empirical from equivalents</td>
<td>1.024</td>
<td>0.0430, wR₂ = 0.0912</td>
<td>0.0572, wR₂ = 0.0976</td>
<td>0.725/-0.677</td>
<td>1552475</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>C₃₆H₃₂N₄O₄:IrCl.C₂H₂Cl₂</td>
<td>765.12</td>
<td>Triclinic</td>
<td>7.9736(2)</td>
<td>14.5144(6)</td>
<td>14.5851(6)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>1451.31(9)</td>
<td>294(2)</td>
<td>P2₁/c</td>
<td>1.751</td>
<td>4.910</td>
<td>752</td>
<td>3.27 to 28.94</td>
<td>10060</td>
<td>6546 [R(int) = 0.0312]</td>
<td>Semi-empirical from equivalents</td>
<td>1.394</td>
<td>1.394, wR₂ = 0.0957</td>
<td>0.0328, wR₂ = 0.0624</td>
<td>1.029/-1.083</td>
<td>1552476</td>
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<tr>
<td>4</td>
<td>C₃₆H₃₁N₄O₄:RuCl.C₂H₂Cl₂</td>
<td>857.78</td>
<td>Monoclinic</td>
<td>10.3125(7)</td>
<td>14.1825(8)</td>
<td>14.0626(7)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>2044.0(2)</td>
<td>292(2)</td>
<td>P2₁</td>
<td>1.394</td>
<td>4.910</td>
<td>868</td>
<td>3.22, 28.81</td>
<td>2044</td>
<td>4680 [R(int) = 0.0590]</td>
<td>Multi scan</td>
<td>1.620</td>
<td>1.620, wR₂ = 0.0912</td>
<td>0.0387, wR₂ = 0.0827</td>
<td>0.48, -0.48</td>
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<td>5</td>
<td>C₃₆H₃₁N₄O₄:IrCl.C₂H₂Cl₂</td>
<td>1033.32</td>
<td>Monoclinic</td>
<td>17.5372(6)</td>
<td>17.5372(6)</td>
<td>16.5079(7)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>2118.86(15)</td>
<td>294.0(3)</td>
<td>Cmc2₁</td>
<td>1.749</td>
<td>13.032</td>
<td>1044</td>
<td>6.032, 52.744</td>
<td>294</td>
<td>4305 [R(int) = 0.0304]</td>
<td>Multi scan</td>
<td>1.749</td>
<td>1.749, wR₂ = 0.0912</td>
<td>0.0387, wR₂ = 0.0827</td>
<td>0.48, -0.48</td>
<td>1552478</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>6</td>
<td>C₃₆H₃₁N₄O₄:IrCl.C₂H₂Cl₂</td>
<td>1205.07</td>
<td>Orthorhombic</td>
<td>14.3694(7)</td>
<td>14.3694(7)</td>
<td>14.3694(7)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>4575.44(4)</td>
<td>292(2)</td>
<td>P2₁/n</td>
<td>1.483</td>
<td>1.620</td>
<td>8034</td>
<td>6.332, 52.744</td>
<td>292</td>
<td>4305 [R(int) = 0.0260]</td>
<td>Gaussian</td>
<td>1.483</td>
<td>1.483, wR₂ = 0.0912</td>
<td>0.0387, wR₂ = 0.0827</td>
<td>0.48, -0.48</td>
<td>1552479</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Structures were refined on F₀²: wR₂ = [Σ[w(F₀² - Fc²)²]/Σw(F₀²)²]¹/², where w = [Σ(F₀²) + (aP)² + bP] and P = [max(F₀², 0) + 2F_c²]/3.

Carboxamide d⁶ metal complexes
Fig. 7.11: Ball and stick representation of the complexes 2 and 3. Hydrogen atoms are omitted for clarity except on amidinato nitrogen.
**Fig. 7.12**: Ball and stick representation of the complexes 4 and 5. Hydrogen atoms are omitted for clarity. The complexes are possessing symmetry with the symmetric operation -x,-y,-z.
Table 7.2: List of selected bond lengths and angles for complexes 2-6.

<table>
<thead>
<tr>
<th></th>
<th>Complex-2</th>
<th>Complex-3</th>
<th>Complex-4</th>
<th>Complex-5</th>
<th>Complex-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-N1</td>
<td>2.085(2)</td>
<td>2.076(3)</td>
<td>2.075(4)</td>
<td>2.086(3)</td>
<td>2.108(9)</td>
</tr>
<tr>
<td>M-N2</td>
<td>2.087(3)</td>
<td>2.092(3)</td>
<td>2.081(3)</td>
<td>2.101(3)</td>
<td>2.051(8)</td>
</tr>
<tr>
<td>M-Cl</td>
<td>2.4186(9)</td>
<td>2.4149(10)</td>
<td>2.4081(13)</td>
<td>2.4237(9)</td>
<td>2.401(3)</td>
</tr>
<tr>
<td>M-Cnt(^a)</td>
<td>1.795</td>
<td>1.785</td>
<td>1.676</td>
<td>1.791</td>
<td>1.765</td>
</tr>
<tr>
<td>C=O</td>
<td>1.241(4)/1.217(4)</td>
<td>1.245(4)/1.226(6)</td>
<td>1.260(6)</td>
<td>1.242(4)</td>
<td>1.261(13)</td>
</tr>
<tr>
<td>N1-M-N2</td>
<td>76.92(10)</td>
<td>76.56(11)</td>
<td>77.16(15)</td>
<td>76.92(11)</td>
<td>76.8(4)</td>
</tr>
<tr>
<td>N1-M-Cl</td>
<td>86.68(8)</td>
<td>84.92(9)</td>
<td>84.67(11)</td>
<td>88.25(8)</td>
<td>84.2(3)</td>
</tr>
<tr>
<td>N2-M-Cl</td>
<td>90.36(8)</td>
<td>88.38(9)</td>
<td>86.11(11)</td>
<td>91.63(7)</td>
<td>87.0(3)</td>
</tr>
</tbody>
</table>

M is ruthenium in complex 6, rhodium in complex 2 and 5 and iridium in complex 3 and 6.

\(^a\) Calculated centroid to metal distances (\(\eta^6\)-Cs/ \(\eta^5\)-Cs coordinated aromatic ring)

The solid-state packing of the complexes shows some intermolecular hydrogen bonds with C-H\(\ldots\)Cl, C-H\(\ldots\)O, C-H\(\ldots\)N and \(\pi\)-\(\pi\) interactions that lead to the building of supramolecular motifs (Figs. 7.14-7.18). Mono-nuclear complexes have exhibited three kinds of intramolecular hydrogen bonding with a bond distance of 2.901 Å, 2.677 Å and 2.314 Å in complex 2 and 2.891 Å, 2.681 Å and 2.307 Å in complex 3 as C-H\(\ldots\)Cl, C-H\(\ldots\)N, C-H\(\ldots\)O interactions respectively. In addition to above interactions in the mono-nuclear complexes (2 and 3), they also contain DCM as a solvent molecule with an interaction to the carbonyl oxygen as C-H\(\ldots\)O with a distance of 2.436 Å and 2.468 Å in complex 2 and 3 respectively (Fig. 7.14 and 7.15). While in di-nuclear complexes such interactions have minimized and the complexes exhibited only shorter C-H\(\ldots\)Cl and a longer C-H\(\ldots\)O/C interaction in comparison to the corresponding interactions of the mononuclear complexes. Complex 4 contains both the interactions with a distance of 2.556 Å as C-H\(\ldots\)O and 2.774 Å as C-H\(\ldots\)Cl (Fig. 7.16). Among the di-nuclear complexes rhodium complex (5) only contains a DCM solvent molecule with a C-H\(\ldots\)Cl interaction in addition to that complex possess only C-H\(\ldots\)Cl interaction (Fig. 7.17). Surprisingly complex 6 has crystallized in a different manner in comparison to the analogue complexes i.e., cis orientation (Fig. 7.18). Such an orientation has reduced all kind of interactions other than C-H\(\ldots\)Cl interaction where both the Cp* and chloride atoms are the same side of the ligand.
Fig. 7.13: Ball and stick representation of the complex 6. Hydrogen atoms are omitted for clarity. The complex is symmetric with the symmetry operation -x,y,z.

Fig. 7.14: H-bonding interactions in complex 2. Hydrogen atoms except for specific positions are removed for clarity.
Fig. 7.15: H-bonding interactions in complex 3. Hydrogen atoms except for specific positions are removed for clarity.

Fig. 7.16: H-bonding interactions in complex 4. Hydrogen atoms except for specific positions are removed for clarity.
Fig. 7.17: H-bonding interactions in complex 5. Hydrogen atoms except for specific positions are removed for clarity.

Fig. 7.18: H-bonding interactions in complex 6. Hydrogen atoms except for specific positions are removed for clarity.
7.4. Conclusions

In summary, we have successfully synthesized six new mono and di-nuclear complexes of p-cymene ruthenium, Cp* rhodium and Cp* Iridium with carboxamide ligand $\text{H}_2\text{L}$. All these neutral complexes are characterized by various spectroscopic studies and complexes 2-6 are additionally supported by X-ray analysis. The ligand under study has formed mono- and di-nuclear complexes predominantly by preferential binding of the metal with the pyridyl nitrogen and deprotonated amidinato nitrogen moieties of the chelating ligand consequently resulting neutral complexes. Though there is a possibility of bonding through oxygen atom of carbonyl group by forming five membered metallacycle by the keto-enol tautomerisation which has been observed in the other complexes but it resulted only through nitrogen of amidato bonded complexes [34]. We are able to isolate complexes 3 and 6 without any deprotonating agent but in the case of other compounds base is necessary to form these neutral complexes.

7.5. References


